Bitumen–Silica Model Composites: The Role of the Filler

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Synopsis

The storage moduli of bitumen–silica model composites obey a simple relationship: $E' = E'_0 + A\phi\psi$, where ϕ is the filler volume ratio and ψ the bitumen–silica interfacial area for a unit volume of composite. This equation is experimentally verified taking various silicas of different surface areas or chemical surface reactivity. The influence of the interface properties on the mechanical glass transition temperature is also examined.

INTRODUCTION

The storage modulus (E'), the loss modulus (E''), and the loss tangent (tan $\delta = E''/E'$) are three characteristics describing the viscoelastic behavior of a material. The amount of mechanical energy dissipated, which is a significant factor for reinforced elastomers, is formally proportional to the square of strain amplitude and to the loss modulus. However, for rubbery compounds, tan δ is generally taken as the most representative parameter since it depends less on the experimental conditions of measurement (amplitude of deformation). Medalia and co-workers[1,2] proposed an empirical relationship between the loss tangent of carbon black–rubber vulcanizates and a loading–interfacial area parameter $\phi\psi$, where ϕ is the volume fraction of filler and ψ the interfacial area: $\psi = S \rho\phi$ (S is the specific surface area of the filler and ρ its specific gravity); hence, $\phi\psi = \phi^2 S\rho$.

This relation was verified at various temperatures (25, 60, and 105°C) under forced vibration conditions, ranging from 0.25 to 1 Hz, at 10–25% double strain amplitude, for a limited range of filler content. Medalia's expression is of practical interest since it helps the compounder to select the best formulation (by choosing the filler content or its surface area) when a given degree of hysteresis (attenuation) is required.

Recently, we[3] developed Medalia's concepts using a different viscoelastic material and another filler, namely, bitumen and silica. The main results were as follows: bitumen has well-defined rheological properties and is relatively easy to handle; pure bitumen follows a typical viscoelastic behavior: it obeys a Williams-Landel-Ferry (WLF) equation (the reference temperature being 298 K); and bitumen–silica composites behave as classical reinforced elastomers: they follow the WLF equation.

Additionally, we have shown, taking the interfacial parameter ($\phi\psi$) as a variable, that an increase in filler content has the same influence on the mechanical

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properties as a temperature decrease or a frequency enhancement (triple equivalence principle). Moreover, a simple relationship between the storage moduli and $\phi\psi$, at given temperature and frequency, has been evidenced:

$$E'(\phi\psi) = E_0' + A\phi\psi$$

The purpose of the present study is to demonstrate the validity of this expression taking either the surface area of the filler or its surface activity as variables. The influence of $\phi\psi$ on the change of the glass transition temperatures of the composites will also be examined.

EXPERIMENTAL

Characterization of the Products

Bitumen

The bitumen 80/100 is a residue of direct distillation [Raffinerie de Feyzin, SNEA(P)]. Its specifications are the following: penetration (ASTM D5–61): 90 (tenth of 10^{-3} m); ring and ball softening point (ASTM 036-26): 48°C; Fraas point (IP 80–53): −17°C; specific density (25°C/water): 1.012.

Its glass transition temperature measured by differential scanning calorimetry (DSC2, Perkin–Elmer) was found to be −34°C.

Silicas

Pyrogenic silicas "Aerosil" (Degussa) were used. These are nonporous spherical particles whose main characteristics are reported in Table I.

The species A130 to A380 belong to the same series of products and should have the same chemical activity. Silica R972, on the contrary, is a A130 which has been modified by addition of dimethyldichlorosilane, which partially blocks the silanol groups present on the surface of the oxyde. Part of the A300 silica was treated with octamethyl cyclotetrasiloxane (D4) (ref. 4) and does not possess, in principle, any active silanol. Species OX50 and MOX170 are of high aluminium content and should not have the same surface (adsorptive) properties as the first series.

TABLE I
Specifications of the Silicas

Silica	Surface area BET (nitrogen adsorption) (m²/g)	Surface area (CTAB adsorption) (m²/g)	Approximative diameter of the primary particles (nm)
A130	130 ± 25	102	16
A150	150 ± 25	125	—
A200	200 ± 25	150	12
A300	300 ± 30	230	7
A380	380 ± 30	300	7
R972	120 ± 30	—	16
OX50	50 ± 15	—	40
MOX170	170 ± 30	—	15
A300 modified by D4	270	—	—

The surface areas of these fillers were determined by nitrogen adsorption and by a procedure[5] in current use for elastomers which consists of adsorbing N-cetyltrimethylammonium bromide (CTAB). Its higher cross section 61.6 Å^2 (instead of 16.2 Å^2 for nitrogen) seems, at first sight, more representative of the molecules constituting bitumen which will be adsorbed onto silica.

Sample Preparation

It was necessary first to agglomerate the pyrogenic silica using a method developed by Chahal and Saint Pierre[6] because of the low value of its apparent density (0.060 g/cm^3) which makes its incorporation into a viscous liquid quite impossible.

Before mixing at 140°C, both the bitumen and the filler were kept at this temperature for $\frac{1}{2}$ hr. Then, a bitumen filler mixing was performed using a disperser (ultra Turrax, Ika Werke, Stauffen, Germany). The resulting slurry was poured into a preheated mold. The leaking mold consists of stacked square steel plates (20 × 20 cm) having a thickness of 0.1 cm. Intermediary plates have a rectangular cut with dimensions of 8 × 13 cm. The bitumen–silica mix is placed in the rectangular volume between two consecutive plates, and sticking of the bituminous compound on the metal is prevented by inserting PTFE sheets of 0.025 cm thickness between the steel plates. The composite is compacted under 540 Pa at 160°C for 5 min. Next, the homogeneity of the silica dispersion in the bitumen matrix is controlled using optical microscopy, as used for usual elastomers.

Samples required for the Rheovibron viscoelastometer consist of parallelepipeds with dimensions ranging from 1 × 3 to 1 × 5 (× 25 mm). They were cut while still wrapped in the Teflon sheets and their extremities were glued to the preheated metal grips to prevent flow before measurement. For the Metravib's examination, only molded cylinders of 9.5–13 mm diameter and 13–25 mm height were necessary.

Measurement Methods

Mechanical Properties

Two viscoelastometers, the Rheovibron DDV II (Toyo Measuring Instruments, Japan) and Metravib (Société Metravib, Ecully, France), were used to assess the dynamic mechanical properties of the composites. In both cases, a sinusoidal strain is applied at one end of the sample while the transmitted stress is recorded on the opposite side. The deformation is controlled, in the case of the Rheovibron by a servo strain gauge and in the case of the Metravib by an electrodynamic exiter. The resulting force is monitored by a gauge.

The Rheovibron permits the application of a given strain, the reading of the stress and the attenuation. The Metravib yields the complex rigidity modulus, the stress and the phase angle. The amplitude of deformation can be adjusted for values of ΔL between 0.1 and 500 μm.

The measurements were performed out at 20°C in a thermostatically controlled room.

In the case of the viscoelastometer Rheovibron, the sample is held horizontally. Creep is important for specimens containing little or no filler which cannot

therefore be submitted to measurement. In order to obtain a representative result, a statistical study is necessary using 20–25 test pieces. Values lying outside $M_1 \pm \sigma$ were discarded when calculating the final mean M_2. The Rheovibron was set to 11 Hz and an amplitude of deformation $2\Delta L = 31.2 \ \mu m$ which resulted in a relative deformation $\Delta L/L$ of 0.06%.

The samples for the Metravib are considerably larger and held in a vertical position. Creep was therefore not observed and no detailed statistical study was necessary. Samples containing little or no filler could also be used, but those with higher concentrations were limited by an extreme value of $|k^*|$ equal to 5 $\times 10^7$ N/m. The same relative amplitude of 0.06% was used as for the Rheovibron. The properties of a number of composites, already determined using the Rheovibron, were confirmed with the Metravib. The two techniques are complementary and give identical results.

Adsorption Capacity

A given amount of asphaltenes (which chemisorb on silica),[7] is dissolved in carbon tetrachloride; 20 ml of the solution are used to treat 1 g silica previously dried at 100°C. The mixture is stirred at 20 ± 0.1°C for 1 hr (a duration sufficient to attain the adsorption equilibrium). Then, the solid residue is recovered by centrifugation washed with hot carbon tetrachloride and air dried to constant weight. The amount of adsorbed asphaltenes is determined as the weight loss of the solid residue during pyrolysis at 800°C.

Experimental Results

Adsorption Studies

Table II gathers the results expressed as the weight of asphaltenes per unit weight and unit surface area of the solid.

Clearly, the first series of silicas have the same adsorption capacity per unit surface area.

On the one hand, the treated silicas (R972, A300 + D4) show a significant lower chemisorption potential than the initial fillers. This is particularly true for Aerosil 300 treated with octamethyl cyclotetrasiloxane which does not fix any appreciable amount of asphaltenes. Indeed, this solid has only about 0.5 free silanol per 10 nm² left[4]: an amount which is shielded by the chemisorbed D4 molecules and does not react with asphaltenes because of steric hindrance.

TABLE II
Irreversible Adsorption of Asphaltenes on Silicas

Silicas	g/g (± 0.01)	g/m² ($\times 10^{-3}$)
A130	0.14	1.08
A150	0.14	0.95
A200	0.17	0.83
A300	0.26	0.87
A380	0.35	0.92
R972	0.03	0.25
A300 + D4	0.00	0.00
OX50	0.08	1.70
MOX170	0.29	1.70

On the other hand, the remaining two silicas possess enhanced adsorption properties, a result which is related to the existence of aluminium surface sites of higher reactivity.

Storage Moduli

The storage moduli of the bitumen–silica composites, measured at 20°C and 15 Hz, are displayed in Figure 1. The values of E' are statistical mean values as mentioned earlier. For the sake of comparison, $\phi\psi$ expressed as m^2/cm^3 are calculated with the values of the surface areas measured by gas adsorption. This of course is not entirely correct since the bitumen–silica interactions are limited by the available or external surface area as measured by CTAB adsorption, for instance. However, CTAB adsorption measurements cannot be performed on the modified or surface-treated silicas since aberrant values are recorded. This remark accounts for the nonzero intercept of the experimental plot discussed elsewhere.[3]

DISCUSSION

Figure 1 verifies the relation $E' = E'_0 + A\phi\psi$ in two manners: E' increases with the specific surface area of the filler, and E' remains constant when $\phi\psi$ is kept constant, i.e., when varying either the filler volume ratio (ϕ) or the specific interfacial area ($\psi = \rho S \phi$) so as to keep the value $\phi\psi$ constant.

Moreover, E' is dependent on the surface activity of the filler. Clearly, the value of E' corresponding to a deactivated surface is lower than the one relative to the initial silica, whereas a higher surface activity leads to a better value of E'. It is worth underlining that the chemical surface treatment does not totally
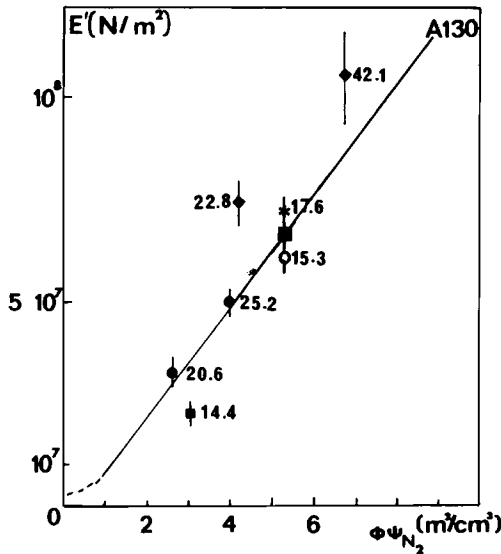

Fig. 1. Storage moduli of silica–bitumen composites in relation with the interfacial parameter $\phi\psi$. Weight fractions are shown near the experimental points. (*) A200, (□) A300, (○) A380, (●) R972, (■) A300 + D4, (◆) OX50 and OX170.

cancel the interaction possibilities, since physical interaction through dispersion forces are certainly taking place.

To summarize, the main points of this study are: the establishment of a simple relationship between E' and an interfacial parameter $\phi\psi$, and the outlining of the influence of the chemical surface activity of the filler.

An increase of E' is probably a consequence of the enhancement of the influence of the interfacial properties or a change of the cohesive properties throughout the bulk of the binder phase. With regular reinforced elastomers, for instance, for the SBR–carbon black system the interface has only a very limited range of influence: its action is restricted to a shell of a few angstroms thickness, where the movements of the chains are perturbed.[8]

The interesting and new situation is that the bulk of the bitumen now appears to be affected. There seems to exist a structuration of the binder induced by the filler. Such a possibility could be demonstrated; indeed, when studying the adsorption of bitumen, from solution onto silica, an ordering of the different constituents of the bitumen around the solid particles was evidenced. First, the asphaltenes or the most polar constituents readily chemisorb on silica, through hydrogen bonding or acid-base interactions. Then, the resins organize themselves around the first layer, and finally the nonpolar parts of the bitumen become involved. Hence, it is understandable that the filler surface properties will play a predominant role even at a large distance from the solid surface.

The study of the bitumen–silica systems presents a further advantage over the classical reinforced vulcanizates which received a great deal of attention: it is not necessary to proceed to crosslinking giving rise to a network with its own characteristics, thus obscuring the contribution of the interfacial properties.

Since silica and bitumen exchange strong interactions, it is reasonable to expect that the cooperative molecular movements of the bitumen units will be restricted. In other terms, it is probable that the interface will manifest its existence by altering the glass transition of the composite.

The mechanical glass transition temperature (T_m) was measured with the Rheovibron operating at a frequency of 11 Hz (value corresponding to the maximum of the plot of the loss moduli versus temperature). Figure 2 indicates
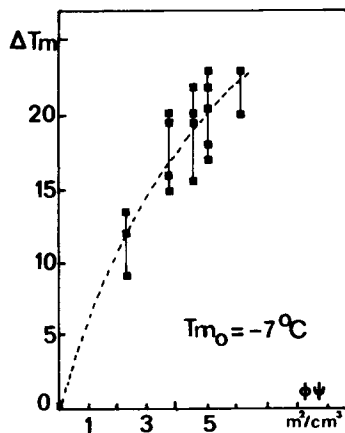

Fig. 2. Mechanical glass transition temperatures of silica–bitumen composites in relation with the interfacial parameter $\phi\psi$.
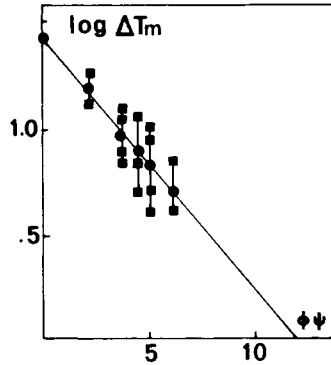
Fig. 3. Mechanical glass transition increment as a function of $\phi\psi$. (■) Measured values, (●) mean values.

the experimental results which again are statistical mean values. A significant increase of T_m, about 20°C, is observed when the interfacial parameter $\phi\psi$ goes from 0 to 7 m²/cm⁻³. T_m levels off for the higher values of $\phi\psi$. The experimental results obey the following relationship (Fig. 3):

$$\log[T_{m,\max} - T_m] = A\phi\psi + \log[T_{m,\max} - T_{m0}]$$

where $T_{m,\max}$ is the highest value of the mechanical glass transition and T_{m0} is the value corresponding to pure bitumen. T_{m0} is equal to $-7°C$.

The above equation is similar to the one evidenced by Droste and Dibenedetto,[9] but for glassy polymers (phenolic resin and glass spheres or clays)

$$T_g - T_{g0} = (T_{gm} - T_{g0})(1 - e^{-B\phi})$$

The fact that T_m reaches a limit is not unexpected, since with increasing filler load, or interfacial area, all the bitumen units will be progressively concerned.

The results of Figure 2 may also be compared to those of Lipatov,[10] who studied the variation of T_g of PMMA or PS filled with silicas

$$T_g = T_{g0} + f\Delta T$$

where ΔT is the maximal increment of T_g for a polymeric phase entirely influenced by the solid surface. ΔT corresponds to $f = 1$; f is related to the particle radius (R) and to the thickness of the immobilized binder layer (ΔR) by

$$f\phi/(1 - \phi) = [(\Delta R + R)/R]^3 - 1$$

Further, f depends on the specific surface area of the filler (S), its surface energy (E_f), the rigidity (r) of the binder, and its cohesion energy (E_c):

$$f = f(S, r, E_c/E_f)$$

In fact, the present study deals with very similar parameters concerning a true viscoelastic composite.

CONCLUSION

The role of the filler in bitumen–silica composites is particularly clear. It creates new linkages between filler and matrix, and it immobilizes increasing amounts of binder molecules, thus augmenting the rigidity of the material and its glass transition temperature.

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